Rotationally Resolved Spectroscopy of SF_6 in Liquid Helium Clusters: A Molecular Probe of Cluster Temperature

M. Hartmann, R. E. Miller,* J. P. Toennies, and A. Vilesov[†]
Max-Planck-Institut für Stromungsforschung, Bunsenstrasse 10, D-37073, Göttingen, Germany
(Received 3 April 1995)

A rotationally resolved infrared spectrum has been obtained for SF_6 molecules captured inside of helium clusters of approximately 4000 atoms. The spectrum is interpreted in terms of a spherical top Hamiltonian, although the resulting rotational constant is considerably smaller than that of free SF_6. This can be attributed to the interaction between the molecule and the surrounding helium liquid. The results indicate that the SF_6 is located inside the helium cluster and a fit to the spectrum yields a rotational temperatures for the perturbed SF_6 of 0.37 ± 0.05 K.

PACS numbers: 67.40.Yv, 33.20.Ea, 36.90.+f

Considerable theoretical [1–4] and experimental [5–9] attention has recently been given to the study of helium clusters, which can provide a unique opportunity for studying quantum systems of finite size. Helium clusters are the only ones that are definitely fluid and, for clusters of approximately 100 atoms or more, are predicted to show superfluid behavior at $T \lesssim 1.9$ K [3,4]. Although most of the usual macroscopic superfluid phenomena are not accessible for study in clusters, several experiments have been proposed for detecting superfluidity in finite systems [10,11]. A potentially powerful approach involves doping helium clusters with weakly interacting neutral atoms or molecules and using spectroscopy to probe the local microscopic environment. Indeed, these doped helium clusters have been the subject of a number of recent experimental [6,9,12–14] and theoretical studies [15–18] studies. As first demonstrated experimentally by Gough *et al.* [19] in 1985, doped argon clusters can easily be formed using a "pick-up" technique in which the pure clusters pass through a secondary beam or gas cell containing the atoms or molecules of interest. The first application of this method to the study of helium clusters was reported in 1990 by Scheidemann *et al.* [6,20]. Since then, a large number of studies have been reported for the capture of various atoms and molecules [6,9,12–14,21] in helium clusters. Recently the cross sections for total scattering [21,22], capture, and coagulation (formation of complexes within the He cluster) [21] have been measured as a function of cluster size. Deflection of the helium clusters due to scattering has also been used to measure the helium cluster size distributions for various source temperatures and pressures [22].

The first infrared spectra of molecules captured by helium clusters were carried out by Goyal, Schutt, and Scoles [14], using SF_6 as the dopant molecule. In these experiments a line tunable CO_2 laser was used to excite the ν_3 vibrational mode of the SF_6. The vibrational bands observed in this was are very narrow, apparently revealing a small splitting of the triple degeneracy in the ν_3 vibrational band. This was taken as evidence that the SF_6 was on the surface of the cluster, since such an asymmetric site is needed to lift the degeneracy associated with the ν_3 vibration. Unfortunately, the line tunable lasers used in this study were not able to provide the complete spectrum needed to obtain more detailed information on the state of the molecule in the cluster.

In a more recent study by Fröchtenicht, Toennies, and Vilesov [12] a diode laser was used to obtain a continuous ν_3 spectrum of SF_6 in helium. This spectrum showed what appeared to be a rotational band contour characteristic of a spherical top. Attempts to fit this spectrum lead to the conclusion that the rotational constant of the SF_6 in helium is considerably smaller than the gas phase value. Since the P and R branches were not resolved in this spectrum, the effective rotational constant of the molecule and the temperature of the cluster could not be accurately determined.

In the present study we report the first rotationally resolved infrared spectrum of a molecule embedded in a liquid helium cluster, from which we obtain both the rotational constants and temperature. Assuming that the rotational degrees of freedom of the molecule have equilibrated to the temperature of the cluster, this being accompanied by evaporation of helium atoms from the cluster following capture of the SF_6 [21], the present experiments gives the first direct measurement of the temperature of a helium cluster. The experimental value is in excellent agreement with theoretical calculations for pure helium clusters, namely, $T \approx 0.32$ K [2].

The apparatus used in this study is shown in Fig. 1. A cluster beam is formed by expanding helium from a 5 μm diameter nozzle, operated at a pressure of 40 bars and a temperature of 20 K. The droplet size can be varied from 10 000 to 1500 atoms [22] by varying temperature of the nozzle. Three differential pumping stages follow the source chamber, with base pressures less than 10^{-7} mbar in the first and 10^{-9} mbar in the mass spectrometer chamber. These low pressures are essential to keep the helium clusters free from molecular

0031-9007/95/75(8)/1566(4)$06.00

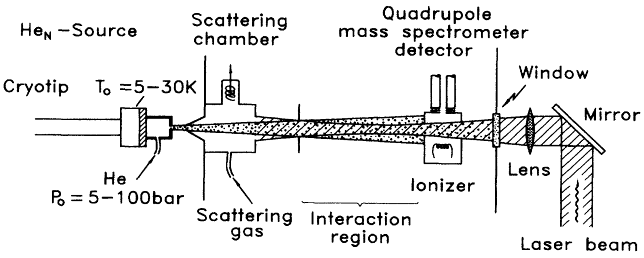

FIG. 1. A schematic diagram of the experimental apparatus.

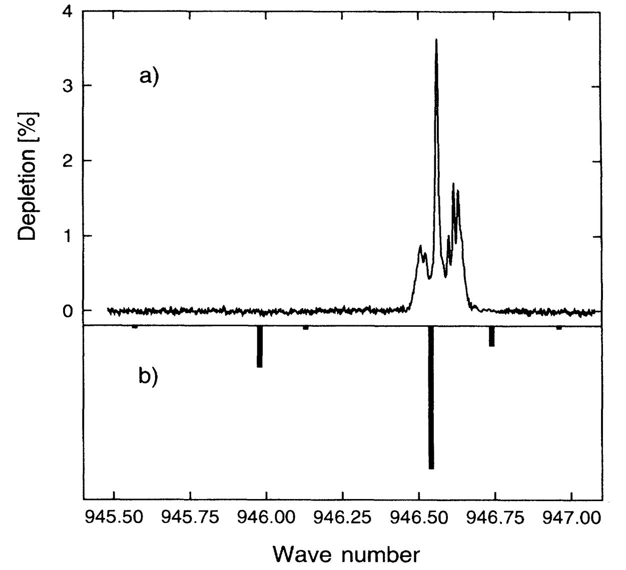

FIG. 2. A continuous scan of the ν_3 vibrational spectrum of SF_6 in helium. The spectrum has been corrected for laser power variations (approximately 10%) over the scan. The bar graph shows the spectrum obtained by Goyal, Schutt, and Scoles [14] using line tunable CO_2 and N_2O lasers. The mean helium cluster size for the conditions used here is $N = 4000$ atoms.

contaminants that are otherwise captured from the background gases in the chamber. The SF_6 pressure in the first of these chambers is adjusted (1×10^{-6} to 5×10^{-5} mbar) to optimize the SF_5^+ signal in the mass spectrometer. After capturing a molecule, the droplets rapidly cool by evaporation [2]. The fact that the detection can be carried out on SF_5^+ implies that during the ionization process all of the helium atoms are lost and the SF_6 undergoes normal dissociative ionization.

A diode laser is used to excite the SF_6 molecules in the helium droplets prior to ionization. Absorption and relaxation of the 10 μm photon results in the loss of approximately 200 helium atoms by thermal evaporation. This resulting recoil of the droplets and the associated decrease in their ionization cross section gives rise to the observed depletion signal. The laser is amplitude modulated at 180 Hz, and the mass spectrometer signals are processed by a lock-in amplifier. The chopper blade was gold coated to time share the laser light between the molecular beam apparatus and an ammonia cell (transition at 946.368 cm^{-1}) and 240 MHz free spectral range air spaced etalon for absolute and relative frequency calibration, respectively.

Figure 2 shows a spectrum of SF_6He_N formed with the nozzle at 20 K, corresponding to a mean cluster size of 4000 atoms [22]. This spectrum resembles that of a spherical top, the central feature being the *Q* branch and the transitions to the high and low frequency sides being the *R* and *P* branches, respectively. The central band is redshifted by 1.415(1) cm^{-1} from the origin of the spectrum of gas phase SF_6 at 947.9763 cm^{-1} [23], a value that is much better determined than in the earlier paper [12]. We purposely scanned the laser well out into the low frequency wing of the main band to look for the second peak reported in the previous study of Goyal, Schutt, and Scoles [14], shown by the bar graph in the figure. This second band is obviously not observed in the present spectrum, indicating that the intensity in this region is at least a factor of 50 lower than the main band. Upon addition of nitrogen gas to the capture cell we observe a band in this region of the spectrum, leading us to conclude that in the previous study of Goyal, Schutt, and Scoles [14] they may have also had nitrogen-SF_6 complexes in their helium clusters. The present results clearly show that the intensity in this region is far less would be expected if the SF_6 occupied a surface site. The lack of observable splittings in the ν_3 vibrational states provides rather conclusive experimental evidence that the SF_6 is in a symmetric environment, presumably inside the cluster. This is in agreement with the theoretical predictions for this system [16,18].

It is important to note that the excited ν_3 vibrational state of SF_6 is triply degenerate and has a large Coriolis coupling constant ($\zeta = 0.69344$ [23]). As a result, the spacing between transitions in the *P* and *R* branches is reduced in comparison with that expected from the inertial rotational constant ($B = 2730$ MHz [23]), namely, $2B(1 - \zeta) = 1674$ MHz. It is evident from the spectrum in Fig. 1 that the spacing is even smaller than this, indicating that the rotational motion of the SF_6 is significantly modified by its interaction with the helium cluster. Since the origin of the Coriolis coupling in SF_6 is the degeneracy of the ν_3 vibration, which the present results indicate is not lifted by the helium, we expect that the Coriolis coupling constant of the SF_6 in the cluster will not be appreciably different from the gas phase value. Given the small vibrational frequency shift, this should be a very good approximation. Also, since the magnitude of the Coriolis term is linear in *J* [23], we expect it to scale linearly with the effective rotational constant. We proceeded to modify an asymmetric rotor program to include the Coriolis coupling constant and the nuclear spin statistics associated with SF_6 [23]. The spectrum was fit with

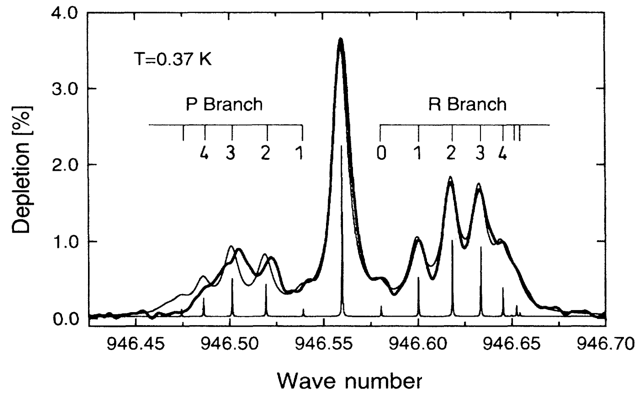

FIG. 3. An expanded view of SF_6He_N spectrum of Fig. 1, showing a fit using a conventional rotor Hamiltonian, including the effects of centrifugal distortion and Coriolis coupling. The underlying stick spectrum was calculated using the same constants as obtained from the fit.

the constraint that the molecule remains a spherical top within the helium cluster.

Figure 3 shows an expanded view of the experimental spectrum shown in Fig. 1 for SF_6He_N ($N \approx 4000$), along with the result of the fit, which for simplicity was generated assuming the ground and excited state constants are equal, namely, $B'' = B' = 1019(30)$ MHz, $D'' = D' = 1.12(8)$ MHz, and $\nu_0 = 946.562(1)$ cm^{-1}. A Lorentzian line shape was used in fitting this spectrum (300 MHz FWHM), a Gaussian giving much poorer agreement with the experimental results. The agreement between the experiment and the calculation is clearly very good, with the only significant differences being in the P branch.

We begin the discussion by considering the rotational temperature of 0.37 ± 0.05 K, the error bar determined by a conservative, subjective assessment of the quality of the fit to the relative intensities of the various P, Q, and R branch transitions. If we assume that the cluster has reached equilibrium after the capture process, this rotational temperature can be taken as the first direct experimental determination of a helium cluster temperature. The theoretical calculation of Brink and Stringari [2] for large clusters yields a temperature of approximately 0.32 K corresponding to the average cooling time characteristic of the present experiment, namely, 0.8 ms. Although this value is within the error bar of the experimental measurement, the difference may be a result of the finite size of the clusters considered here [2].

As noted above, the rotational constant obtained from the observed spectrum is smaller than that of gas phase SF_6. One way of interpreting this result is that a number of helium atoms are "rigidly" attached to the SF_6, thus increasing its effective moment of inertia. To test this idea, the principle moments of inertia were calculated for a number of rigid SF_6He_N complexes. The helium atoms were placed at a distance from the center of the SF_6 molecule determined from the peak in the radial density function of Whaley [1], namely 4.5 Å, resulting in the solid triangles in Fig. 4. The solid square is the result of a calculation for eight helium atoms using the potential of Pack *et al.* [24]. Calculations were performed for cluster sizes that maintain the spherical symmetry, namely, $n = 6$, 8, 12, and 18. Based on this simple rigid model, the experimental rotational constant is consistent with somewhere between 6 and 8 helium atoms rotating with the SF_6, depending upon which bond length is chosen. Given that the global minima on the He-SF_6 potential of Pack *et al.* [24] are the eight, threefold sites, the concept of a "frozen" layer of eight helium atoms around the central SF_6 molecule, embedded in a liquid helium cluster, is rather appealing. This is particularly true given that Whaley [1] interprets the sharpness of the first peak in the radial density profile around the SF_6 as an indication that the first solvation shell is frozen. However, the latter calculations give 22–23 helium atoms in this frozen shell, which corresponds to a rotational constant much smaller than the value determined here.

Although this rigid model for the first solvation shell gives a rather appealing and simple explanation for the present results, the concept of a "rigid" helium complex is somewhat of an oxymoron. Perhaps a more reasonable explanation is that the helium atoms are undergoing some dynamical exchange, such as in the occupancy of the threefold sites. In such a picture the slowing down of the rotational motion of the SF_6 could be interpreted as resulting from the SF_6 molecule effectively tunneling between various local minima on the potential surface created by the nearby helium atoms. Manz [25] has described a very similar phenomenon in matrices in terms of pseudorotation of the cage, which can also account for the increase in the moment of inertia. Unfortunately, neither the present experiments nor the theoretical work

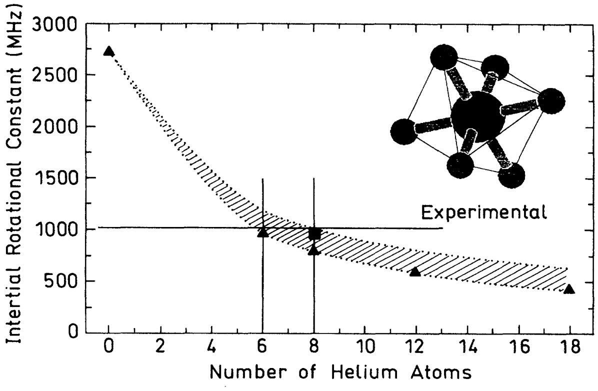

FIG. 4. A comparison between the calculated rotational constants for different numbers of rigidly attached helium atoms and the experimental result [1019(30) MHz]. The solid triangles correspond to a S-He distance of 4.5 Å while the solid square was calculated based upon an estimate of the S-He distance from Pack *et al.* [24]. Overall, the experimental rotational constant is consistent with 6–8 attached helium atoms. The inset shows an SF_6 molecule with its eight threefold sites.

that has been done to date can distinguish between these models.

It is interesting to note that the centrifugal distortion constant obtained from the present fit is 4 orders of magnitude larger than the value for gas phase SF_6, the latter being 1.66×10^{-4} MHz [23]. The implication is that this distortion is associated with the helium atom motions, which we have already shown to be coupled to the SF_6 rotation. It is interesting to note that the pseudorotation theory of Manz [25] predicts "the faster the rotation of a matrix-isolated molecule, the smaller should be the cage's pseudorotational ability to follow the rotation; i.e., we predict increasing effective rotational constants with increasing rotational quantum number." This is exactly the opposite of what is observed here.

If the Lorentzian linewidth of 300 MHz is interpreted as a measure of some vibrational relaxation rate in the cluster, the result is a lifetime of 525 ps. In light of all the work that has been done on the vibrational predissociation rates of small binary and ternary complexes [26], this value is not at all unreasonable. Nevertheless, caution must be exercised here since there are several other ways of interpreting this width for the present case. For example, the overall rotational motion of the helium complex could be a contributing factor to the broadening. Alternatively, the width would be interpreted as a dephasing process, analogous to collisional broadening in the gas phase. Finally, the influence of cluster size on these spectra has not been explored in detail. Since the clusters observed here are not size selected, this could also contribute an inhomogeneous component to the linewidth. Further experimental and theoretical work will be needed before this width can be uniquely assigned to a given mechanism.

In the present study we have made use of a diode laser based, molecular beam apparatus to obtain the first rotationally assigned infrared spectra of a molecular probe in a liquid helium cluster consisting of approximately 4000 atoms. The results provide the first experimental evidence that the cluster temperature is 0.37 K, in good agreement with the theory, and that they are sufficiently cold to be superfluid [3,4]. The rotational constants associated with the SF_6He_N cluster are consistent with approximately eight helium atoms rigidly attached to the molecular frame. At present, however, it is unclear whether this frozen cluster picture of the system is reasonable or not. Further experiments and theory will be needed to determine the proper way of interpreting these data. Work is presently underway to study the cluster size dependence of these spectra, as well as to study higher order $(SF_6)_N He_N$ and $X_M SF_6 He_N$ clusters.

The authors are grateful to Dr. R. Fröchtenicht for his contributions in the early stages of this work and to M. Behrens for his technical assistance. The authors are also thankful to Professor U. Buck and Dr. M. Lewerenz for many valuable discussions. M.H. and A.V. thank the DFG for financial support and R.E.M. is grateful to the NSF (Grant No. CHE-93-18936) for partial support.

---

*Alexander von Humboldt-Stiftung Senior U.S. Scientist. Permanent address: Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599.

†On leave from Institute of Physics, St. Petersburg State University, 198904 St. Petersburg, Russian Federation.

[1] K.B. Whaley, Int. Rev. Phys. Chem. **13**, 41 (1994).
[2] D.M. Brink and S. Stringari, Z. Phys. D **15**, 257 (1990).
[3] P. Sindzingre, M.L. Klein, and D.M. Ceperley, Phys. Rev. Lett. **63**, 1601 (1989).
[4] M.V. Rama Krishna and K.B. Whaley, Phys. Rev. Lett. **64**, 1126 (1990).
[5] J. Gspann and H. Vollmar, J. Chem. Phys. **73**, 1657 (1980).
[6] A. Scheidemann, J.P. Toennies, and J.A. Northby, Phys. Rev. Lett. **64**, 1899 (1990).
[7] H. Buchenau, E.L. Knuth, J. Northby, J.P. Toennies, and C. Winkler, J. Chem. Phys. **92**, 6875 (1990).
[8] K. Martini, J.P. Toennies, and C. Winkler , Chem. Phys. Lett. **178**, 429 (1991).
[9] S. Goyal, D.L. Schutt, and G. Scoles, J. Phys. Chem. **97**, 2236 (1993).
[10] J.W. Halley, C.E. Campbell, C.F. Giese, and K. Goetz, Phys. Rev. Lett. **71**, 2429 (1993).
[11] M. Lewenstein and L. You, Phys. Rev. Lett. **71**, 1339 (1993).
[12] R. Fröchtenicht, J.P. Toennies, and A. Vilesov, Chem. Phys. Lett. **229**, 1 (1994).
[13] A. Scheidemann, B. Schilling, and J.P. Toennies, J. Phys. Chem **97**, 2128 (1993).
[14] S. Goyal, D.L. Schutt, and G. Scoles, Phys. Rev. Lett. **69**, 933 (1992).
[15] M.V. Rama Krishna and K.B. Whaley, J. Chem. Phys. **93**, 6738 (1990).
[16] R.N. Barnett and K.B. Whaley, J. Chem. Phys. **99**, 9730 (1993).
[17] E. Dalfovo, Z. Phys. D **29**, 61 (1994).
[18] E. Krotscheck and S.A. Chin, Chem. Phys. Lett. **227**, 143 (1994).
[19] T.E. Gough, M. Mengel, P.A. Rowntree, and G. Scoles, J. Chem. Phys. **83**, 4958 (1985).
[20] A. Scheidemann, B. Schilling, J.P. Toennies, and J.A. Northby, Physica (Amsterdam) **165B**, 135 (1990).
[21] M. Lewerenz, B. Schilling, and J.P. Toennies, J. Chem. Phys. **102**, 8191 (1995).
[22] M. Lewerenz, B. Schilling, and J.P. Toennies, Chem. Phys. Lett. **206**, 381 (1993).
[23] B. Bobin, C.J. Borde, J. Borde, and C. Breant, J. Mol. Spectrosc. **121**, 91 (1987).
[24] R.T. Pack, E. Piper, G.A. Pfeffer, and J.P. Toennies, J. Chem. Phys. **80**, 4940 (1984).
[25] J. Manz, J. Am. Chem. Soc. **102**, 1802 (1980).
[26] R.E. Miller, Science **240**, 447 (1988).